PYRITE IN AN EH3 METAL-SULFIDE NODULE S. W. Lehner[1], P. Nemeth[1], M. I. Petaev[2] P. R. Buseck[1]; [1]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, (slehner@asu.edu, pbuseck@asu.edu); [2]Department of Earth & Planetary Sciences, Harvard University, Solar, Stellar, & Planetary Sciences, Harvard-Smithsonian CfA, Cambridge, MA 02138, (mpetaev@fas.harvard.edu).

Introduction: There is substantial evidence in EH chondrites for gas-solid sulfidation whereby ferromagnesian silicates were replaced by silica, niningerite, troilite, and oldhamite [1-4]. These reactions are clearly documented in a subset of EH3 ferromagnesian chondrules containing abundant cristobalite, S-rich porous silica, niningerite, and troilite, hereafter called sulfidized chondrules [4]. The S-rich porous silica, which is amorphous and whose microprobe analyses indicate up to 5 wt% S and several wt% Na, Ca, or Mg, is a clear indicator of these replacement reactions. S-rich porous silica similar to that in the sulfidized chondrules is also common in the cores of metal-sulfide nodules (MSNs) [5].

Phase relations within the sulfidized chondrules suggests silicates could have been sulfidized in a H-depleted, dust-enriched, environment with the fS_2 buffered by an Fe-FeS melt [4, 6]. MSNs, which presumably formed under similar conditions [7], consist predominantly of Fe,Ni metal and troilite [3, 8-10], and may thus contain clues to the nature of the sulfidizing environment. One such MSN with a porous-silica core in the EH3 chondrite ALH 84170 contains pyrite and is the subject of this report.

Methods: Chemical mapping and EDS analyses of the MSN were performed using an FEI XL-30 SEM with a FEG source. A TEM section was extracted with a focused-ion beam (FIB) using an FEI NOVA dual-source SEM. TEM, STEM, EDS, and electron diffraction were performed using JEOL 2010F, 2000, and 4000 microscopes. EDS data were quantified using the Cliff-Lorimer thin-film approximation with theoretical k-factors.

Observations: Minerals adjacent to the MSN core include troilite, niningerite, schreibersite, and zincian daubreelite (Fig. 1). Fibrous strands of Fe- and S-rich material within the porous silica core have a S/Fe ratio of ~2 (Figs. 2 and 3). Minor schreibersite and porous silica also occur near the periphery of the nodule. Perryite occurs randomly within the kamacite and at the kamacite interface with troilite.

The feathery S- and Fe-rich features evident in backscattered SEM images (Figs. 2, 3) consist of fine-grained Fe-sulfides. Some areas are predominantly pyrite (Fig. 4 inset), although most appear to be mixtures of pyrite and pyrrhotite. These fine-grained sulfides are situated in a groundmass of porous silica containing ~1 to 16 wt% S; from 1 to 2 wt % of Ca, or rarely, Na; up to 2 wt% Fe; and ~ 1 wt% Cl.

The co-existence of kamacite, troilite, pyrrhotite, and pyrite testifies to disequilibrium (Fig. 5) within the MSN. Because its mantle is mainly a mixture of kamacite and troilite (Fig. 1), local fS_2 during its solidification was likely close to the Fe-FeS buffer. Pyrite and pyrrhotite in the core of the nodule require higher fS_2, temperatures below the pyrite stability limit (1016 K), and physical separation from Fe metal. At subsolidus temperatures, the pyrrhotite- and pyrite-bearing silica was probably isolated by the metal-troilite mantle so an external source of sulfur is unlikely. In addition, external S would react with kamacite to form troilite. Therefore, the source of S is presumably internal, most likely a S-rich gas trapped within the porous silica. Its fS_2 was likely close to that of the Fe-FeS buffer at the quenching temperature. If that temperature was equal to the metal-troilite eutectic (vertical red line in Fig. 5), then the fS_2 in the trapped gas was ~10^{-7} bar (horizontal red line in Fig.5). At such fS_2 values, pyrrhotite and pyrite can only be stable below ~850 K and ~700 K, respectively, which lie within the range of metamorphic temperatures recorded in EH3 sulfides [6, 16].

These observations suggest that pyrrhotite and pyrite likely formed within silica vesicles by reaction of troilite with S-rich gas released from the porous silica during shock reheating of the EH3 parent body. Why and how S-rich gas was dissolved in the SiO_2-rich melt that formed the porous silica remains to be understood. A plausible scenario would require formation of S-rich porous silica at pressures significantly exceeding those of a classic solar nebula.

Conclusions: The occurrence of S-rich, porous silica enclosing pyrrhotite and pyrite in the core of an MSN points to local disequilibrium, perhaps caused by rapid fluctuations of temperature and pressure. That the fS_2 was sufficient to stabilize these phases is consistent with MSN having been processed in a sulfidizing environment.

References: [1] Rubin A. E. (1983) *E&PSL* 64: 201-212. [2] Grossman et al., 1985 *GCA* 49: 1781-1795. [3] Ikeda, Y. (1989) *Proc. NIPR Symp.Antarctic Meteor*. 2: 109-146. [[4] Lehner S. W. et al. (2013) *GCA* 101: 34-56. [5] Lehner et al. (2011) *LPI Workshop on form. of first solids in the SS* Abst. 9079. [6] Guillermet A. F. et al. (1980) *Metall. Trans.*, 12B, 745-754. [7] Lehner et al. (2012) *LPSC 43* #2252 [87] Weisberg and Prinz (1998) *LPSC 29* #1741. [9] Lin and El Goresy, (2002) *MAPS* 37: 577-599. [10] Lehner et al. (2010) *MAPS* 45: 289-303.

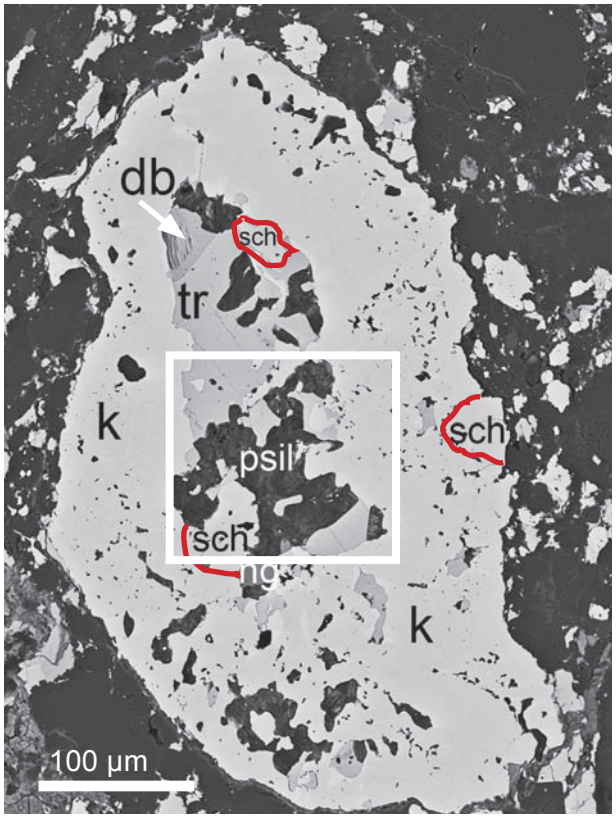

Fig. 1. (A) BSE image of an MSN with S-rich porous silica core. The rectangle is enlarged in Fig 2. k = kamacite, tr = troilite, ng = niningerite, sch = schreibersite (within red lines), psil = porous silica.

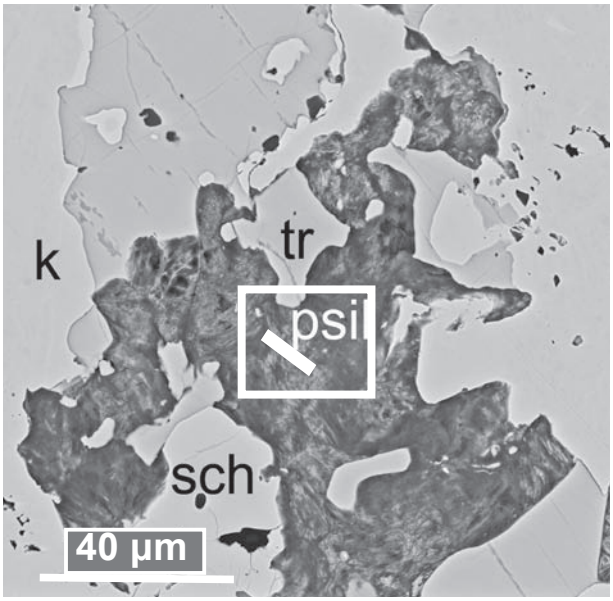

Fig. 2. BSE image of the center of the MSN in Fig 1. The bright areas have a S/Fe ratio of ~2. The white line markes the ~ location of the FIB liftout. Abbreviations as in Fig.1

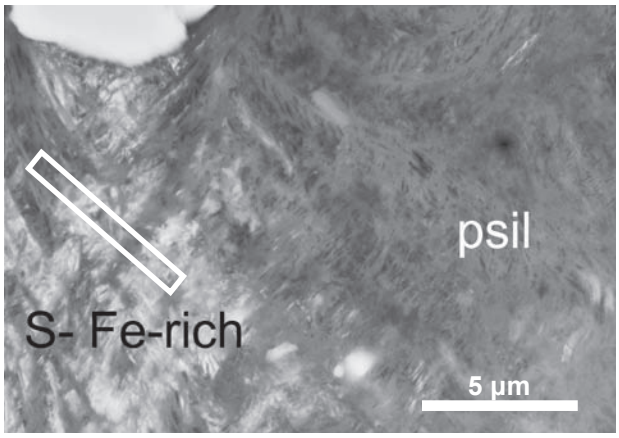

Fig. 3. BSE enlargement of the rectangle from Fig. 2 showing the feathery porous texture. The white rectangle markes the ~location if the FIB liftout. Abbreviations as in Fig.1

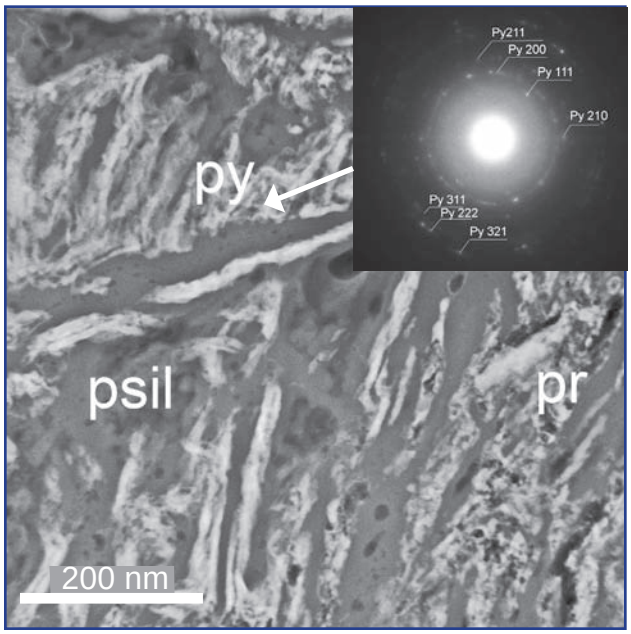

Fig. 4. Scanning TEM annular dark-field image of a portion of the FIB section marked in Fig. 3. Sulfides are the bright areas enclosed within porous silica. py = pyrite, pr = pyrrhotite, Other abbreviations as in Fig.1

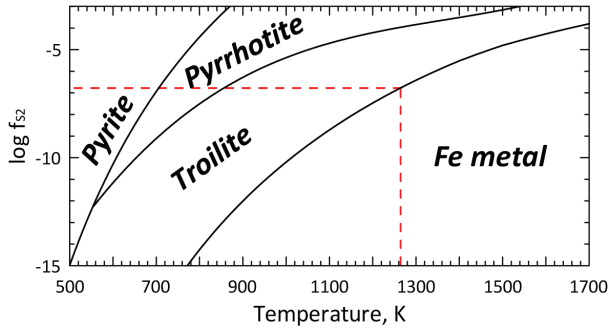

Fig. 5. Stability fields of Fe metal, troilite (FeS), pyrrhotite ($Fe_{0.877}S$), and pyrite (FeS_2). Dashed red lines show the Fe-FeS eutectic temperature and corresponding fugacity of S_2 gas.